Table 6 Dynamic high temperature water extraction of selected polycyclic aromatic hydrocarbons from an urban air particulate reference material (NIST 1649)[a]

Compound	*Certified concentration* $\mu g\ g^{-1}$ *(%RSD)*	*Estimated concentration as % of certified concentration (%RSD) (n = 3)*[b]
Fluoranthene	7.0 (7)	134.0 (16)
Pyrene	7.2 (7)	87.5 (15)
Benzo[*a*]pyrene	2.9 (17)	72.0 (29)

[a] Reference: Daimon H and Pawliszyn J (1996) *Analytical Communications* 33: 421.
[b] High temperature water extraction: 250°C and 50 atm.

sealed by crimping with an appropriate cap, e.g. an open-centred aluminium cap containing a PTFE/grey-butyl moulded septum. In order to promote the release of volatiles a small quantity of water (10–30%) may be added to the soil sample. In addition, the volatility of an analyte can be increased by heating the sample. This can simply be done by placing the sealed sample vial in a thermostatically-controlled water bath. It has been suggested that at ambient temperature this headspace SPME approach can be effective for three ring PAH compounds or more volatile compounds.

Conclusion

While SPME has been applied to a wide range of application areas, it is those with an environmental theme that have been mainly used to date. The main focus of this article is on the method of operation for a range of sample types. Specific examples have been provided as to the application of SPME for extraction of analytes from aqueous and solid matrices. In addition, the different forms of analysis from aqueous samples are considered, i.e. direct and headspace sampling while for solid samples, the use of a slurry technique, prior to hot water extraction and headspace SPME is considered. The experimental data provided should act only as a guide to the potential and diverse applications of SPME.

See also: **II/Chromatography: Gas:** Headspace Gas Chromatography. **III/Environmental Applications:** Soxhlet Extraction.

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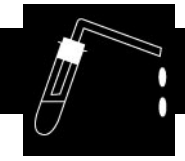
SOLVENTS: DISTILLATION



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Introduction

In modern chemical analysis various physicochemical methods are used to achieve high detection sensitivity. In trace analysis, reported detection levels are often measured in $\mu g\ mL^{-1}$ (ppm) $ng\ mL^{-1}$ (ppb), as well as in $pg\ mL^{-1}$ (ppt). Achievement of such low detection levels has been made possible by the use of modern analytical instruments equipped with new types of detectors and by improved sample preparation methods. Both factors are closely related to the purity of the solvents used as the mobile phases in different variants of liquid chromatography (LC), capillary zone electrophoresis (CZE), liquid–liquid (LLE) and solid-phase (SPE) extraction, filtration and flotation. Moreover, high-purity solvents are also employed to dilute samples investigated using chromatography, spectral and electrochemical analysis. Thus, solvents used in chemical analysis must fulfil many physicochemical requirements.

High-purity solvents, for example for liquid chromatography (LC) and/or for spectroscopy, are produced by many manufacturers. However, purification and quality testing of solvents are often necessary before use, particularly in the above-mentioned techniques

applicable to multicomponent systems. For instance, the mobile phases in LC, CZE and SPE are often modified by different organic and/or inorganic salts.

In this article the most important physicochemical properties of commonly used solvents are briefly reviewed, including methods of their purification, recovery and quality testing.

Solvents: Properties and their Usage

In many cases the purity of the solvents used has a great influence on whether the molecular processes occurring in a multicomponent system proceed in the desired manner. The quality of measured data can often be improved by using high-purity solvents. For chromatography or spectroscopy a good solvent is characterized by high purity, and in consequence, by low values characterizing the transparency (cut-off) and refraction (refractive index). Parameters such as reactivity and good miscibility are also important criteria for solvent selection. In LC investigations, multicomponent solvents which have low boiling points (between 20 and 60°C) and low viscosity ($\eta < 50$ cP) are preferred. A good solvent should be able to dissolve the sample, although this is seldom a problem in analytical separations when the mobile phase has the correct strength.

The important physical parameters characterizing the most commonly used solvents in many analytical techniques are listed in **Table 1**. On the basis of this table it can be seen that LC is the most frequently applied technique and consequently it consumes a large amount of the various solvents. A high usage of solvents in LC results from the various separation modes of this technique.

In normal-phase (adsorption) liquid chromatography (NPLC) aliphatic hydrocarbons (e.g. *n*-hexane, *n*-heptane) are usually used as the mobile phase. The elution strength of these solvents is often modified by other organic compounds. A fundamental problem with NPLC eluents is the presence of dissolved water and trace amounts of the higher-fraction olefines. These contaminations can cause changes in the cut-off values (UV detection, spectrophotometry), baseline perturbation and poor reproducibility of retention data. Halogenated solvents such as dichloromethane can react with other reactive organic solvents (e.g. acetonitrile) and form crystalline products.

In reversed-phase liquid chromatography (RP-LC) aqueous solutions of methanol, acetonitrile, tetrahydrofuran and dioxan are used as eluents. In this mode of LC the most serious problem, besides the purity of the organic modifiers in the mobile phase, is the

Table 1 Properties of solvents used in various analytical techniques

Solvent	*UV-cut-off (nm)*	*Refractive index (25°C)*	*Boiling point (°C)*	*η (25°C) (cP)*	*ε (20°C)*
Acetone	330	1.356	56	0.30	20.70
Acetonitrile	190	1.341	82	0.34	37.50
Benzene	280	1.498	80	0.60	2.30
n-Butanol	210	1.397	118	2.60	17.52
Carbon tetrachloride	265	1.457	77	0.90	2.24
Chloroform	245	1.443	61	0.53	4.80
Cyclohexane	200	1.423	81	0.90	2.02
Cyclopentane	200	1.404	78	0.42	1.97
Diethyl ether	218	1.350	35	0.24	4.30
Dimethylformamide	268	1.428	153	0.80	36.73
Dimethylsulfoxide	268	1.477	189	2.00	4.70
Dioxane	215	1.420	101	1.22	2.21
Ethanol	210	1.359	78	1.08	24.60
n-Heptane	195	1.385	98	0.40	1.92
n-Hexane	190	1.372	69	0.30	1.88
Isooctane	197	1.389	99	0.47	1.94
Methanol	205	1.326	65	0.54	32.71
Methylene chloride	233	1.421	40	0.41	8.93
n-Octanol	205	1.427	195	7.31	10.30
n-Pentane	195	1.355	36	0.22	1.84
i-Propanol	205	1.384	84	1.90	20.30
n-Propanol	240	1.385	97	1.90	20.30
Tetrahydrofuran	212	1.405	66	0.46	7.56
Toluene	285	1.494	110	0.55	2.40
Water		1.333	100	0.89	80.00

η, viscosity; ε, dielectric constant.

purity of the water, which may contain trace impurities of phenols, hydrocarbons, etc. Tetrahydrofuran is frequently used as the solvent in gel permeation chromatography (GPC). It must be stabilized by butylate hydroxytoluene (BHT), which is used as an antioxidant. However, in ion suppression and ion pair RP-LC the mobile phases are often modified by the addition of compounds which can change the dissociation constants of analytes, such as inorganic and organic acids or ionic substances (e.g. ammonium chloride, cetyl chloride). All these components may contain inconvenient impurities which can also crystallize, causing some perturbation in detection during the elution process. As a result of these impurities extra peaks may appear in the chromatograms, making identification of the substances analysed more difficult. The impurities may interfere with the analyte's retention even if a UV-transparent mobile phase (e.g. methanol–water, acetonitrile–water and/or ethanol–water) is used.

Figure 1 shows the peak heights of different compositions of solvent gradually decreasing from their cut-off limits to become very low or almost negligible at wavelengths larger than 320 nm.

Another factor which influences the separation process and which may result from solvent impurities during chromatographic elution is peak tailing and/or peak splitting. In solid-phase extraction (SPE) irreversible sorption of solvent impurities on active sites of packing materials (e.g. surface silanols or chemically bounded ligands with polar groups such as –OH, $-NH_2$, –CN, etc.) can be manifested by relatively high differences in reproducibility of recoveries.

Therefore, before chromatographic or spectroscopic measurements are made, a special preparation (e.g. isolation, purification and preconcentration) of the sample is recommended. For this purpose techniques such as LLE, SPE, filtration and membrane separation are used. It should be mentioned that high-purity solvents are required to prepare analytical samples.

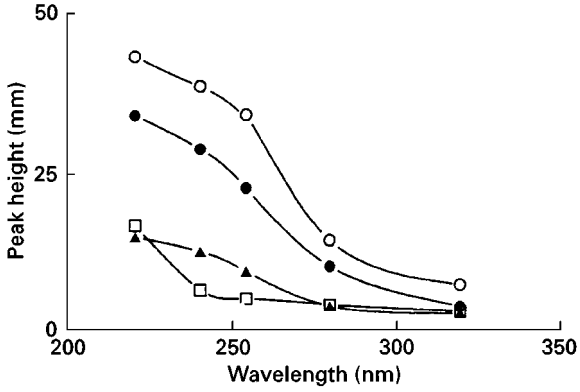

Figure 1 Plot of peak heights versus wavelength of radiation in the UV spectrophotometer for the mobile phase methanol (analytical grade) – water (home purified) at compositions 30 : 70% (v/v) (○), 50 : 50% (v/v) (●) and 70 : 30% (v/v) (▲), and composition 50 : 50% (v/v) (□) prepared from LC-grade solvents (J. T. Baker, Deventer, The Netherlands). (Reproduced with permission from Buszewski, Bleha and Berek (1985).)

Methods of Solvent Purification

There are many methods of solvent purification, but the most common are simple distillation, fractional distillation and steam distillation. A recent method of solvent purification using solid-state packing materials is becoming more popular. It can be carried out by LC, SPE, filtration, and ultrafiltration utilizing membranes.

Distillation

Distillation is the oldest and simplest procedure for solvent purification, and it is also inexpensive. It is based on Raoult's law, which states that the partial vapour pressure of a solvent is proportional to its mole fraction. The physical foundations of separation by distillation depend on the distribution of constituents between the liquid and the vapour phases being at equilibrium. In general, the composition of the vapour is different from the composition of the distillate. Only azeotropic mixtures distill without a change in their composition. However, during distillation of a normal mixture the principal component with the lowest boiling point distils first, followed by compounds with higher boiling points. The effectiveness of distillation depends on the physical properties of the components in the mixture, the equipment used and the method chosen.

Simple distillation Simple distillation refers to the process in which molecules transferred from the liquid phase to the vapour phase are not subjected to partial condensation or contact with the condensed liquid prior to reaching the condenser. The composition of the vapour near the liquid phase does not change as it moves toward the condenser. In this technique, equipment requirements are minimal; usually a flask fitted with a condenser and a product receiver are sufficient.

Fractional distillation Fractional distillation is used when a more efficient separation process than simple distillation is required. This type of distillation is an equilibrium process in which the composition of the distillate is constantly changing as the distillation proceeds. The main element of the apparatus is the distillation column, which consists of a series of

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plates placed one above the other in a suitable tube. The column is placed under the receiver. Liquid evaporating from one (lower) plate condenses on the next (higher) plate, where it again evaporates. On each plate an equilibrium between the liquid and the vapour is established. Vapour enriched in more volatile components flows upwards, whereas vapour enriched in less volatile components flows downwards. The performance of the column increases with an increasing number of plates.

Steam distillation Steam distillation is a simple distillation procedure in which evaporation of the mixture is achieved either by continuously blowing steam through the mixture or by boiling water and the sample together. If the sample contains both hydrophobic and hydrophilic components, two layers of distillate develop. In typical steam distillation two layers can be recovered individually. Aqueous distillation seems to provide the best compromise between time, cost and effort.

In many cases satisfactory results are achieved by using distillation for solvent purification. Water used in LC investigations should normally not be purchased, but should be prepared by the user. An inexpensive and easy laboratory procedure for water purification is as follows: deionized water with added alkaline solution of $KMnO_4$ is left for a few days, and then the solution is distilled twice in an apparatus made of hard glass. The conductivity of water purified in this fashion is 10^{-6} S m^{-1}.

In **Figure 2**, plots of absorbance for three combinations of water and methanol mixtures of various purities are shown. The main source of UV absorption by the binary mobile phase was evidently impurities in the methanol. A comparison of the two bottom curves shown in Figure 2 proves the effectiveness of water purification by distillation.

Other solvents, such as aliphatic and aromatic hydrocarbons, alcohols, ethers, tetrahydrofuran and halogenated solvents, can also be purified using distillation methods. However, in many cases the solvent impurities, e.g. water in aliphatic hydrocarbons or halogenated solvents, can make distillation less efficient. In these cases it is necessary to use more effective methods for solvent purification.

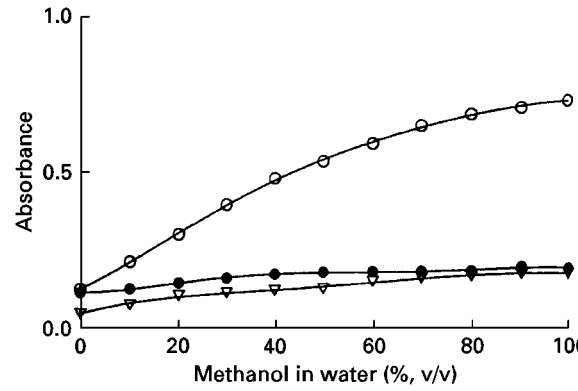

Figure 2 Plot of absorbance for mixtures of water and methanol at 254 nm versus the composition of the solution obtained on the basis of spectrophotometric data using a 3 cm quartz cuvette. Key: ▽, methanol (analytical grade) and water (home purified); ●, methanol (LC grade, J. T. Baker, Deventer, The Netherlands) and water (home purified); and ○, water and methanol (LC grade, J. T. Baker). (Reproduced with permission from Buszewski, Bleha and Berek (1985).)

Adsorption Methods

In adsorption chromatography (NPLC), control of the water content in the solvents is important. In some cases it is preferred to mix known amounts of dry and water-saturated solvents together in order to know the percentage of water saturation. Generally, analytical grade purity solvents should not contain impurities. On the other hand, the addition of activated molecular sieve beads (0.4 or 0.5 nm in diameter) to the flask with the solvents clearly improves their purity and reduces the water content. Various impurities, in addition to water, can be often removed by adsorption methods, particularly frontal analysis, which is often utilized in LC.

In this method a glass column packed with small adsorbant particles (0.15-0.2 mm in diameter), usually dried silica gel or alumina oxide, is used (**Figure 3**). Before solvent purification the column is heated at 473 K for 8 h under vacuum conditions (10^{-3} Torr) to remove physically adsorbed water. After this operation, unpurified solvent is injected into the column using a syphon-type injector. The purified solvent is collected in a solvent receiver equipped with a moisture trap.

During LC investigations purification and stabilization of the mobile phase is frequently carried out on precolumns. These columns are located between the solvent reservoir and the injector valve. SPE, in conjunction with frontal analysis, is also used for solvent clear-up. It is mainly used for purifying small amounts of solvents, particularly for sample dilution.

Filtration and Membrane Techniques

A reliable and easy laboratory technique for solvent purification is filtration. The mobile phase containing added buffers or reagents may be filtered through a filter (0.5 μm mesh or smaller) to remove particulate matter which can damage the system. The equipment for filtration is very simple, generally consisting of an Erlenmayer flask connected to vacuum and

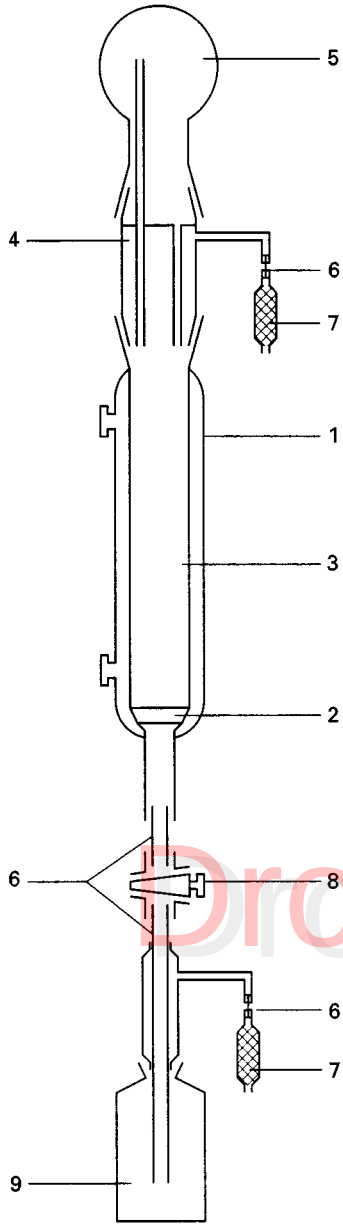

Figure 3 Apparatus for solvent purification. 1, glass column with cooling jacket; 2, glass sinter; 3, silica gel or alumina adsorbent; 4, syphon-type injector; 5, container for unpurified solvent; 6, PTFE tube; 7, moisture trap; 8, valve; 9, receiver for purified solvent. (Reproduced with permission from Buszewski, Lodkowski and Trocewicz (1987).)

a reservoir, in which a porous filter disc or membrane is placed. The porous discs are usually made from nonporous spherical glass beads (1–2 μm in diameter) and/or PTFE. Membranes are usually made from PTFE, cellulose or nylon. To improve the efficiency of the separation process, the surface of the filter discs or membrane is often modified chemically, as are the packing materials, with chemically bonded phases in RP-LC and/or SPE. In this case the surface properties (hydrophobic or hydrophilic) of filters and/or membranes determine the degree of purification.

Water may be purified satisfactorily using a compact water purification system that combines filtration, deionization and charcoal treatment in a convenient, high-volume unit.

Ultrafiltration Ultrafiltration is the other alternative to filtration, where large molecules are separated from solution by using membranes. Membranes are commercially available for separation molecules with relative molecular masses in the range 10^3–10^6. Ultrafiltration is primarily used for the isolation of low- or high-molecular mass substances from different solvents. **Figure 4** shows a comparison of the efficiency of acetonitrile purification utilizing frontal analysis combined with ultrafiltration.

Reverse osmosis Reverse osmosis is similar to ultrafiltration except that membranes of a much smaller pore diameter are employed and the operating pressure is much higher. The operating pressure must exceed the natural osmotic pressure. This technique has been successfully applied to the purification of water and organic solvents.

Dialysis In dialysis, solvents are purified by differential diffusion through membranes under a concentration gradient. The overall efficiency of this process is controlled by the ratio of the flow rates and the properties of membrane, fluid channel and local fluid velocity.

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Recovery and Quality Control

After the purification process or before using solvents in various analytical techniques, quality control is necessary. For this reason, many different analytical

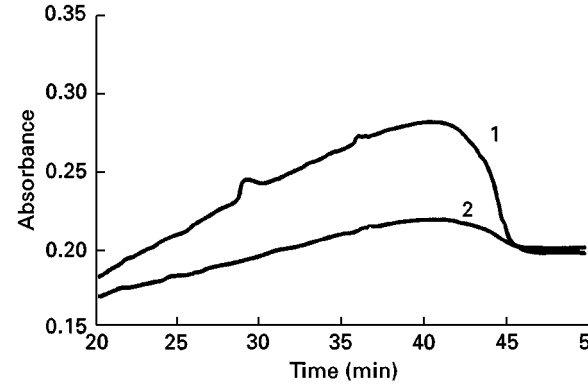

Figure 4 Liquid chromatograms with UV detection using acetonitrile as the mobile phase purified through (1) frontal analysis and (2) ultrafiltration.

Table 2 Concentration of water and difference in absorbance for cut-off (ΔA) of solvents before (C_b) and after (C_a) purification

Solvent	ΔA *(% v/v)*	C_b *(mg L^{-1})*	C_a *(mg L^{-1})*
Acetonitrile A	69.7	2216.0	167.0
Acetonitrile B	10.2	297.0	143.0
Benzene	24.6	308.0	27.5
Cyclohexane	16.8	49.0	4.5
n-Heptane	21.3	18.8	7.7
n-Hexane	17.2	19.6	8.6
Methanol A	77.05	650.0	134.0
Methanol B	3.6	120.0	114.0
Tetrahydrofuran	61.3	1081.0	32.6
Toluene	23.1	167.0	10.0

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methods have been utilized for measuring the characteristic parameters. Generally, chromatographic techniques such as gas chromatography (GC), LC, thin-layer chromatography (TLC) have been used, but ultraviolet (UV), infra-red (IR) and nuclear magnetic resonance (NMR) spectroscopy can also be applied. Water in many organic solvents is usually determined by Karl Fischer titration. On the basis of experimental data obtained before and after purification the efficiency of the clean-up procedure is determined. In general, the efficiency of purification process, e.g. the recovery, is expressed by the coefficient R. This parameter is defined as the ratio of the volume or concentration of removed impurities to the volume or concentration of solvent before purification:

$$R \pm \sigma = (V_a \pm \sigma_a)(V_b \pm \sigma_b) \times 100\% \text{ (v/v)} \quad [1]$$

or:

$$R \pm \sigma = (C_a \pm \sigma_a)(C_b \pm \sigma_b) \times 100\% \text{ (v/v)} \quad [2]$$

where V_a, C_a and V_b, C_b denote volume or concentration of the removed impurities and solvent samples, respectively, and $\sigma, \sigma_a, \sigma_b$ are individual standard deviations.

Table 2 summarizes the results of solvent purification by frontal analysis. In each case, purification of the solvent improves its absorbance at the cut-off point (ΔA).

The small improvement found in the case of the LC grade methanol B is as expected for this high-purity solvent. The high impurity (absorbance difference, $\Delta A = 77.5\%$) of analytical grade methanol A precludes its use in LC investigations. Similarly, toluene, benzene, tetrahydrofuran and acetonitrile A cannot be used in LC measurements without prior purification.

Recovery values for the purification of water, acetonitrile, alcohols, ketones, aliphatic and aromatic hydrocarbons obtained in distillation methods are usually in the range 85–95% (v/v). In the case of halogenated solvents this range is narrower, i.e. 75–80% (v/v). Utilizing membrane techniques for solvent clear-up, it is possible to obtain recovery in the range 90–97% (v/v).

See also: **II/Distillation:** Laboratory Scale Distillation. **Membrane Separations:** Filtration. **III/Flash Chromatography.**

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SORBENT SELECTION FOR SOLID-PHASE EXTRACTION

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Solid-phase extraction (SPE) is a method of sample preparation that concentrates and purifies analytes from solution by sorption onto a disposable solid-phase cartridge, followed by elution of the analyte